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CARBONATE TREATMENT OF U_3O_8 PRECIPITATES

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TOPICAL REPORT A-49

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Work performed under Contract No. W-7405-Eng-85

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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Attached is Topical Report A-49 entitled "Carbonate Treatment of 803 Precipitates" by Gilman Y. Murray and John Dasher. This report describes work conducted by Mr. Murray for a course in Advanced Mineral Dressing and in partial fulfillment of the requirements for the degree of Master of Science in Metallurgy from the Massachusetts Institute of Technology. The course was given by Professor A. M. Gaudin, our Director. As in the case of Mr. Sollenberger's report (Topical Report A-38) Mr. Murray completed the first draft before leaving our group last February, but is not available now to sign the final copy.

Precipitation of simple leach solutions, obtained from 396-5 ore, with magnesia gives a precipitate which contains only 2 per cent 803. Even the solutions from cyclic tests give precipitates which contain only 4 per cent 803. Although these precipitates represent a concentration ratio of over 100:1, they were not considered to be a suitable final product for shipment to existing plants of the Atomic Energy Commission. It is known that X forms a soluble complex ion with sodium carbonate. This reaction is rather specific. If treatment of the low-grade precipitate with a reasonable excess of sodium carbonate would result in extraction of the 803 contained, we would have a simple, inexpensive method of getting the 803 into suitable form for shipment. The tests in this report show that most of the 803 in the precipitates can be extracted with reasonable quantities of sodium carbonate; however, extraction of over 90 per cent of the 803 was not obtained consistently under any of the conditions tried.

In an attempt to find the reasons for poor extractions, tests were run on precipitates from various synthetic solutions containing 803 alone and with ferrous and ferric iron, aluminum and magnesia. The results of the experiments on precipitates from artificial solutions are also inconsistent, and complete extractions were not consistently obtained.

The results are sufficiently good to be promising, and test work is being continued.

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CARBONATE TREATMENT OF 803 PRECIPITATES

By

Gilman Y. Murray and John Dasher

I. INTRODUCTION

This is a report on preliminary attempts to refine a low-grade precipitate of 803 by treatment with carbonate solutions.

Extraction of 803 from 396 ores may be accomplished by leaching with cold, dilute, ferric sulfate and sulfuric acid. The 803 in the resulting leach solution can then be precipitated with any one of several alkalies such as sodium hydroxide, ammonia, calcium oxide, or magnesium oxide. A precipitate of most desirable characteristics is obtained by using magnesia as the precipitant, but this precipitate will settle to only 10 per cent solids, filter to 25 per cent solids, and, when oven-dried, still contains 25 to 35 per cent water of hydration. The oven-dried product usually contains from 2 to 3 per cent 803, and greater percentages of iron, aluminum, silicon and magnesium. This cake contains about 150 pounds of water per pound of 803. If dried it would contain 30 pounds of other oxides per pound of 803. This latter product contains precipitated iron, some of which may be needed in the leaching process. If sodium hydroxide or ammonia is used as a precipitant, the precipitate settles to 1 per cent solids, or less, and if lime is used, the precipitate will be almost half gypsum.

It would be desirable to treat the 803 precipitate in such a way that the resulting product would have a high content of 803. The object of this investigation was to study the treatment of low-grade 803 precipitates with sodium carbonate to redissolve the 803 while leaving the major contaminating elements insoluble. Uranium is known to form a soluble complex ion with carbonate - $UO_2(CO_3)_3$. As this reaction is rather specific for uranium, the method was considered promising.

The investigation was started by treating 803 precipitates from liquors obtained by leaching the 396-5 and 396-50 ores. When this treatment did not proceed satisfactorily, the work on precipitates from the leach liquors was halted temporarily, and artificial solutions of 803 were used to obtain precipitates for retreatment. These artificial solutions also contained ferrous, ferric, magnesium or aluminum ions along with the 803.

II. SUMMARY AND CONCLUSIONS

Precipitates were obtained by neutralizing leach liquors or artificial solutions containing some of the major constituents of leach liquors with magnesia, ammonia, sodium hydroxide, or sodium carbonate. The resultant precipitates were treated with various water-soluble carbonates under different conditions in an attempt to dissolve the uranium contained. A few tests were run in which the precipitates were oxidized and acidified to pH 3 followed by carbonate treatment of the resulting solution.

This attack has not solved the problem. In a few of the tests on the simpler artificial systems, over 90 per cent of the uranium was dissolved in carbonate solutions, but in most of the tests the uranium extraction was 10 to 80 per cent. Although there are many seeming inconsistencies in the data, some implications were noted which may be helpful in the continued investigation of this problem.

The synthetic 803 and ferric-iron solution, when precipitated with ammonia, yielded a precipitate which, upon agitation for eighteen hours with a small amount of sodium carbonate, gave complete extraction of 803. Precipitates from 803-ferrous-iron solutions did not give good extraction with sodium carbonate except after 4 days' agitation. Oxidation of ferrous iron by aeration did not consistently improve the extraction of 803 from precipitates. None of the few tests run on precipitates from artificial solutions containing magnesium or aluminum gave good extractions. Tests on precipitates from leach liquors gave extractions of less than half the 803 when treated with sodium carbonate for 24 hours.

With the exception of the last few tests, the maximum agitation time for carbonate leaching of precipitates was 24 hours. This was thought to be an adequate time; however, the last few tests indicated that the reaction rate between the carbonate and 803 in the precipitate is extremely slow. If this is so, many of the tests might have given complete 803 extraction with a four- to eight-fold increase in agitation time.

Usually, better extraction of 803 by carbonate was obtained in treating precipitates made with ammonia than in treating those obtained with magnesia.

Heat slightly increased the extraction of 803 from precipitates by means of carbonate.

After oxidation of iron by aeration, the acid treatment of the precipitate at pH 3 for 17.5 hours resulted in 70 to 77 per cent extraction of 803 while rejecting most of the impurities. Subsequent carbonate treatment recovered 60 to 100 per cent of this amount while effecting additional purification.

III. EXPERIMENTAL METHODS

Preparation of 803 Solutions

The artificial 803 solutions were made by dissolving uranyl sulfate ($UO_2 \cdot SO_4 \cdot 3\frac{1}{2}H_2O$) in sulfuric acid and diluting to the strength desired. Other ions were also obtained from c.p. sulfates, except for some of the tests in which the ferric iron was obtained from c.p. ferric ammonium sulfate.

The leach liquors used in this investigation were obtained by leaching 396-50 ores with sulfuric acid and Ferrisul. Charges of ore (2.5 kg.) were ground in an Abbé pebble mill at 67 per cent solids to about 80 per cent minus 200 mesh. The ground ore was leached for 24 hours with a pulp density of 50 per cent solids using 20 pounds of sulfuric acid and 10 pounds of Ferrisul per ton of ore. Leaching was done in glass carboys which were agitated on rolls. The leached ore was filtered and washed by repulping three times with distilled water and filtering after each repulping. The pregnant and wash solutions were combined to give a total volume of approximately ten liters.

Precipitation Procedure

Precipitation was carried out on 500-milliliter samples of leach liquor, except where otherwise specified. The solution was mechanically agitated with a glass stirring rod in an 800-milliliter beaker. The pH readings were taken continuously by a MacBeth pH meter. When magnesia or lime was used as the precipitant, small portions were weighed out and made into slurries. Successive portions of these slurries were added to the leach liquor until the desired pH was reached. Concentrated solutions of sodium hydroxide or ammonia were added dropwise from a burette. Except where otherwise noted, the total precipitation time was from ten to fifteen minutes.

Precipitate Dewatering Procedure

Usually the precipitates were allowed to settle to a thick pulp and the clear liquor was decanted, but some of the precipitates were filtered. The thickened pulp or filter cake was then weighed.

Carbonate Treatment Procedure

Sodium carbonate was added to the wet precipitate as a 5.5 per cent solution except in a few preliminary tests where a 6.5 per cent solution was used. The sodium bicarbonate and ammonium carbonate were added as 4.33 and 5 per cent solutions respectively. The pH of the pulp was taken after the carbonate addition. Then the pulp was transferred to closed bottles and agitated on rolls. After the desired agitation period, the pulp was filtered on Büchner filter and the residue washed.

IV. ANALYSES OF LEACH LIQUORS, PRECIPITATES, AND PRECIPITANTS

A typical leach-liquor analysis from 396-5 ore is as follows: 0.104 gram SO_3, 0.25 gram ferric iron, 1.23 gram ferrous iron, 0.48 gram silica, and 0.28 gram alumina per liter. This leach liquor was precipitated by neutralizing to pH 7 with Dow sea-water magnesia (L-2-35). The precipitate obtained, after drying at 105°C, has the following analysis: 2.2 per cent SO_3, 35 per cent iron as ferric oxide, 10.5 per cent magnesia, 10.5 per cent alumina, 10.7 per cent silica, and 28.2 per cent ignition loss.

Analysis of an ammonia precipitate of the 396-50 leach liquor was similar to the foregoing precipitate analysis except that there was no magnesia.

The spectrographic analysis of the 396-50 leach liquor was as follows:

Major constituents -- Fe, Ca, Si, Mg, and Al.
Minor constituents -- Mn, Cu, Ni, Co, Ti, Cr, Sr, and V.

The analyses of the two Dow sea-water magnesias used were as follows:

	L-2-35	L-2-75
	%	%
MgO	83.3	96.7
CaO	1.08	2.25
NaCl	4.5	0.26
SO_4	1.3	0.59
Ignition Loss	9.2	0.59

V. EXPERIMENTAL WORK ON CARBONATE TREATMENT

Precipitates from an Artificial 803 Solution

The leach liquor from the ore is a very complex system. To study the reactions of 803 and carbonate, it is best to start with simple systems and work up to more complex systems.

The simplest system is an artificial solution of uranyl sulfate. Data in Table 1 (Test ARTM2) shows that gradual addition of sodium carbonate to an artificial uranyl sulfate solution raised the pH from 1.75 to 10.0 without the formation of any precipitate.

Table 1. Carbonate Treatment of Artificial 803 Solution

Test No.	Solution Analysis g/l 803	Initial pH	Na_2CO_3 Added (grams)	Final pH	Agitation Time (minutes)	Remarks
ART M2	0.10	1.75	3.03	10.0	40	No ppt. formed.

In two other tests using artificial 803 solutions, precipitates were made with ammonia and magnesia and then treated with sodium carbonate. Results are shown in Table 2. Test ART M12 shows the result of precipitating the 803 solution with ammonia and treating the precipitate with sodium carbonate. The precipitate was a cloudy, yellow colloid which settled after 66 hours to a compact wet precipitate. The water was removed by decantation. Sodium carbonate solution was added to the precipitate and the solution agitated for 24 hours, but there still remained a little cloudy material which did not go into solution. These fine particles were filtered off, but not washed. The resulting filtrate contained only 67.8 per cent of the 803 in the original precipitate. This indicates that the rate of reaction of carbonate with the precipitate is slow.

In Test ARTM13 the same procedure was followed, except that the precipitating reagent was magnesia. Less 803 was precipitated from the leach liquor, but the 803 extraction from the precipitate increased to 78 per cent.

Precipitates from an Artificial 803 and Ferric-Iron Solution

The leach liquors from the leaching of ores 396-5 and 396-50 contain approximately 1.2 grams ferrous iron per liter and 0.2 gram ferric iron per liter. As the carbonate treatment of precipitates from these liquors did not give complete extraction of 803, the next system studied was an artificial solution of 803 and ferric iron. The artificial solution was made from ferric ammonium sulfate and uranyl sulfate and its iron content was 0.4 gram per liter, or one-third as much iron as is present in leach

liquors from ores. In leach liquors from ores, however, the iron is predominantly ferrous. Table 3 shows the data from the first series of tests using an artificial 803 and ferric-iron solution.

Complete extraction of the 803 was obtained from the ammonia precipitate of the 803 and ferric-iron solution with as little as 8 equivalents of sodium carbonate per equivalent of 803. Reduction of the amount of carbonate to 2 equivalents resulted in only 46.5 per cent extraction of 803 from this ammonia precipitate.

When the artificial solution was precipitated with magnesia (Dow L-2-35), the 803 in the resulting precipitate was not readily dissolved by the carbonate. As seen in Table 3, Test ART M8, the extraction of 803 in the sodium carbonate solution was only 43.9 per cent compared to the complete extraction obtained in Test ART M6A, a similar test, in which ammonia was the precipitating reagent. This comparison indicates that magnesia is harmful to the extraction of the 803 precipitate by sodium carbonate.

In Table 4, two tests are shown in which another artificial 803 and ferric-iron solution was precipitated with sodium hydroxide and the precipitate treated with sodium carbonate.

This new artificial solution was made from ferric sulfate, with a three-fold increase in ferric iron concentration to 1.14 grams per liter. Tests ART M31 and ART M32 were run on this solution with sodium hydroxide as the precipitating reagent. Addition of 32 equivalents of sodium carbonate to the thickened precipitates gave 82.9 and 81.9 per cent 803 extraction respectively, as shown in Table 4. The decrease in extraction to 82.9 per cent from complete extraction (Test ART M6A, Table 3) might be attributed either to the use of NaOH in place of NH_4OH or to the increased ratio of iron to 803.

Tests ART M28 and ART M29, Table 5, were run using the same artificial 803 and ferric-iron solutions described above. The solution was precipitated with sodium carbonate and agitated for one hour. Presumably the 803 was in solution but other elements were precipitated as hydroxides or carbonates. In Test ART M28 the precipitate was settled one hour and filtered. The filtrate contained only 53.1 per cent of the 803. In Test ART M29, the precipitated pulp was agitated 24 hours before filtering. This filtrate contained 66.6 per cent of the 803. The 803 extractions in these tests were lower than in the tests where sodium carbonate was added after ammonia or sodium hydroxide were used as the precipitating reagents. The low extractions in these tests may have been the result of using a pH of 8.0 during carbonate agitation instead of a pH of 9 or more as in the tests where complete extraction of 803 was attained. Moreover, in the dilute pulps of Tests ART M28 and ART M29 the carbonate concentration was low.

Table 2. Carbonate Treatment of Precipitate from Artificial 803 Solution

Test No.	Solution Analysis g/l 803	Fe^{++}	Fe^{+++}	Precipitation Reagent	pH	Agitation Time (Hours) 1/	% of 803 Ppt. 2/	Ppt. Wet Wt. g.	Retreatment Na_2CO_3 g.	Equiv.	pH	Agitation Time (Hours)	Extraction of 803, %
ART M12	0.1	0	0	NH_4OH	8.7	4.3	95.4	6	1.76	32		24	67.8
ART M13	0.1	0	0	MgO	10.85	4.0	76.0	6	1.76	32		24	78.0

*Artificial solutions contained uranyl sulfate equivalent to 0.1 g. per liter 803. The precipitates formed were colloidal. The solutions were settled sixty-six hours and decanted.

Table 3. Carbonate Treatment of Ammonia and Magnesia Precipitates

ART M6A	0.102	0	0.4	NH_4OH	6.85		56.0	1.76	32	10.2	18	107.1
ART M6B	0.102	0	0.4	NH_4OH	7.4		59.0	0.44	8	9.3	18	102.1
ART M11	0.102	0	0.4	NH_4OH	7.15		55.0	0.33	6	9.1	21	85.8
ART M7B	0.102	0	0.4	NH_4OH	7.0		65.0	0.22	4	8.75	18	77.8
ART M6C	0.102	0	0.4	NH_4OH	7.1		75.0	0.11	2	8.3	18	46.5
ART M8	0.102	0	0.4	MgO	9.45		15.0	1.76	32	11.1	18	43.9
ART M9	0.102	0	0.4	MgO	8.0		25.0	0.44	8	10.75	16	27.6

Table 4. Carbonate Treatment of Sodium Hydroxide Precipitate of 803 and Ferric Iron

ART M31	0.103	0.05	1.14	NaOH	7.6		158.0	1.76	32	11.2	18	82.9
ART M38	0.103	0.05	1.14	NaOH	7.4		228.5	1.76	32	11.2	16.5	81.9

Table 5. Precipitation of Artificial 803 and Ferric-Iron Solution with Sodium Carbonate

ART M28	0.103	0.05	1.14	Na_2CO_3	8.0	1	578	4.30 3/		8.0	0	53.1
ART M29	0.103	0.05	1.14	Na_2CO_3	8.0	1	580	4.39 3/		8.0	24	66.6

1/ In tests where no data are given on agitation time it was between 5 and 15 minutes.
2/ In tests where the completeness of 803 precipitation is not given it was not determined, but assumed to be over 95 per cent on the basis of previously reported test work.
3/ This weight of sodium carbonate was added for the original precipitation and not as a retreatment.

Precipitates from an Artificial 803 and Ferrous Iron Solution

The extraction of 803 by carbonate from precipitates obtained from 803 and ferrous iron solutions was also studied.

In addition to its function as a solvent for 803, sodium carbonate was employed as the precipitating reagent for iron and other elements, in the three tests on these solutions. Data are given in Table 6. The test in which the largest amount of sodium carbonate was added after pH 7 had been reached (ART M23) gave the best 803 extraction. Much of the carbonate added to the acid solution was utilized in neutralizing the excess acid present. Although Test ART M24 had a 24 hour agitation period after the pH reached 7.0, the extraction of 803 in the carbonate solution was slightly lower than in Test ART M23, which had only a 45-minute agitation period.

The artificial 803 and ferrous iron solution was precipitated with ammonia or sodium hydroxide. Precipitates were retreated with carbonate as shown in Table 7. The extraction of 803 from an ammonia precipitate of 803 and ferrous iron by sodium carbonate increased from 45.5 per cent to 70.0 per cent as a result of increasing the amount of sodium carbonate. The 500-milliliter sample of artificial solution used in Tests ART M10A and ART M10B contained 0.05 gram 803 and 0.65 gram ferrous iron. By stoichiometry, 1.1 grams sodium carbonate is needed per gram 803 and 1.9 grams per gram iron. Therefore, the sodium carbonate necessary to react with the 803 in this solution is 0.055 gram, and with the iron 1.24 grams -- a total of 1.295 grams. In Test ART M10A, 1.4 times and in Test ART M10B, 2.1 times, the stoichiometric equivalent for both 803 and iron was used.

As complete extraction of the 803 was not achieved in either test, it may be concluded that precipitation of ferrous carbonate is not wholly responsible for poor extraction. It is conceivable that a ferrous uranate might be formed, and that it might be very slowly soluble in sodium carbonate.

In Tests ART M30 and ART M37, in which sodium hydroxide was employed as the precipitant the 803 extraction from the precipitate was 84.5 per cent. This extraction is nearly twice as high as that in Test ART M10A. These tests indicate that the 803 precipitated with sodium hydroxide reacts more readily with the carbonate than the 803 in a similar precipitate obtained with ammonia.

Table 6. Precipitation with Sodium Carbonate of Artificial 803 and Ferrous Iron Solutions

Test No.	Solution Analysis g/l 803	Fe++	Fe+++	Precipitation Reagent	g.	pH	Carbonate Retreatment Additonal Carbonate g.	Equiv.	pH	Agitation Time (Hours)	% 803 in Solution
ART M3	0.099	1.3	0	Na_2CO_3	2.33	7.0	0.44	*	7.2	1.75	30.9
ART M23	0.090	1.05	0.07	Na_2CO_3	1.18	6.9	1.43	*	8.05	0.7	48.6
ART M24	0.090	1.05	0.07	Na_2CO_3	1.65	6.7	0.96	*	7.9	24.0	43.1

*Carbonate agitation time for ART M23 considered from time pH of pulp reaches 7.0 until agitation stopped. The precipitate was not thickened. Equivalents not calculated due to neutralization.

Table 7. Carbonate Treatment of Ammonia and Sodium Hydroxide Precipitates from Artificial 803 and Ferrous Iron Solutions

Test No.	Solution Analysis g/l 803	Fe++	Fe+++	Precipitation Reagent	pH	Ppt. Wet Wt. g.	Carbonate Retreatment Na_2CO_3 g.	Equiv.	pH	Agitation Time (Hours)	Extraction of 803 %
ART M10A	0.10	1.3	0	NH_4OH	7.0	26.5	1.80	33	10.85	24	45.5
ART M10B	0.10	1.3	0	NH_4OH	7.0	35.0	2.70	49	11.8	24	70.0
ART M30	0.090	1.05	0.07	NaOH	7.3	63.5	1.76	35	11.45	18	84.5
ART M37	0.090	1.05	0.07	NaOH	7.0	109.0	1.76	35	11.0	17	84.5

Heat was employed in a series of tests, as seen in Table 8, to speed up the reaction of the sodium carbonate with the 803 in the precipitate. At room temperature, the extraction of 803 in Test ART M10A was 45.5 per cent; at 67°C, 64.2 per cent; and at 90°C, 77.3 per cent. In the last test the carbonate solution evaporated to dryness during the night. The residue was repulped in distilled water and agitated for two hours at 90°C. These tests indicate that heat helps to speed up the reaction of 803 with carbonate. The poor extraction in Test ART M40 may have been due to the short agitation period with sodium carbonate.

As it is possible that the reaction rate is slow, two tests were run on precipitates from artificial solutions in which the precipitates were given a long sodium carbonate agitation period. These are compared with a shorter test in Table 9.

Tests with long leaching periods gave extractions of 803 as high as 96.3 per cent. The extraction more than doubled with an increase of carbonate agitation time from one day to four days. This indicates a slow reaction rate. Further testing is certainly indicated.

Air-Oxidized Precipitates from an Artificial 803 and Ferrous Iron Solution

Since the carbonate extraction of 803 from ferric iron and 803 precipitates was higher than from ferrous iron and 803 precipitates under similar conditions, an investigation was made in which the 803-ferrous iron precipitate was air-oxidized before the carbonate treatment.

Test ART M25 was run to determine the completeness of the air oxidation of the ferrous iron to ferric. Aeration for 20 hours with the pH between 6.8 and 7.9 resulted in complete oxidation of the ferrous iron.

Table 10 shows the results of Tests ART M17, ART M16, and ART M14, which were run using magnesia, sodium hydroxide and ammonia, respectively, as precipitants. After air oxidation, the thickened precipitates were treated with sodium carbonate. The poorest 803 extraction was obtained in the test which employed magnesia as the precipitating reagent. In the other two tests the sodium hydroxide precipitate of 803 yielded a slightly higher 803 extraction than the ammonia precipitate. None of the extractions was good.

As 803 is more soluble in bicarbonate than in carbonate solution, two tests were run to see if bicarbonate improved 803 extraction. Results are shown in Table 11. An extraction of 51.3 per cent of the 803 was obtained from an oxidized precipitate treated with sodium carbonate, but the oxidized precipitate treated with sodium bicarbonate gave an extraction of 70.4 per cent. These tests indicate that sodium bicarbonate may be the better reagent for dissolving the 803 from the precipitate.

Table 8. Effect of Heat on Sodium Carbonate Treatment of 803 - Ferrous Iron Precipitates

Test No.	Solution Analysis g/l 803	Fe++	Fe+++	Precipitation Reagent	pH	Ppt. Wet Wt. g.	Aeration Time (Hours)	Carbonate Retreatment Na_2CO_3 g.	Equiv.	°C	pH	Agitation Time (Hours)	Extraction of 803, %
ART M10A	0.10	1.3	0.	NH_4OH	6.9	26.5		1.80	36	Room Temp.	10.85	24	45.5
ART M34	0.09	1.05	0.07	NH_4OH	7.0	89.0		1.76	35	67	10.5	18	64.2
ART M36	0.09	1.05	0.07	NH_4OH	7.05	41.0		1.76	35	90	10.8	18	77.3
ART M40	0.09	1.05	0.07	NH_4OH	7.1	46.5		3.52	72	100*	--	2	2.5

NOTE: ART M36 evaporated to dryness after sixteen hours, 120 ml. distilled water added, agitated two hours.
*ART M40 heated in boiling water bath.

Table 9. Effect of Long Agitation Period on Sodium Carbonate Treatment of 803 - Ferrous Iron Precipitates

ART M10A	0.090	1.05	0.07	NH_4OH	7.0	26.5		1.80	36		10.85	24	45.5
ART M42A	0.090	1.05	0.07	NH_4OH	7.0	47.5		1.76	35		10.7	94	96.3
ART M42B	0.090	1.05	0.07	NH_4OH	7.5	56.9		1.76	35		10.7	164	89.6

Table 10. Carbonate Treatment of Air-Oxidized Precipitates from an Artificial 803 and Ferrous Iron Solution Using Different Precipitating Reagents

ART M17	0.10	1.2	0	MgO	6.65	19.0	17*	1.76	32		11.2	22	12.5
ART M16	0.10	1.2	0	NaOH	7.3	107.0	22	1.76	32		11.3	22	57.3
ART M14	0.10	1.2	0	NH_4OH	7.5	63.0	22	1.76	32		10.2	22	51.3

*pH after aeration 10.0.

Table 11. Carbonate Treatment of Air-Oxidized Precipitates from Artificial 803 and Ferrous Iron Solution Using Sodium Carbonate and Sodium Bicarbonate

ART M14	0.10	1.2	0	NH_4OH	7.0	63.0	22	1.76	32		10.2	22	51.3
ART M15	0.10	1.2	0	NH_4OH	7.5	58.0	22	1.38 1/	32		7.95	22	70.4

1/ Sodium Bicarbonate.

The tests shown in Table 12 were run with and without the air oxidation step. The aeration step caused a reduction in 803 extraction from 84.5 per cent to 57.3 per cent. The indication is that the aeration step is harmful to the extraction of 803 by carbonate. Perhaps the iron should be oxidized before neutralization. This could be done with sulfur dioxide and air.

Table 13 shows the results of aerating, not aerating, and drying an ammonia precipitate of 803 and ferrous iron, before treating with sodium carbonate. In these tests, the extraction of 803 by carbonate was highest on precipitates which had been oxidized with air. This is the opposite to what took place with a sodium hydroxide precipitate of 803 and ferrous iron. It was thought that drying the precipitate before treating it with carbonate might cause a change in solubility. However, as seen in Table 13, the extraction in Test ART M35 was only 50.7 per cent, so it is indicated that the drying step had little effect on the extraction of the 803.

Precipitates from Artificial Solutions Containing Magnesium and Aluminum

A few tests were run on artificial solutions to which either magnesium or aluminum had been added. Table 14 shows the results of these tests. Tests ART M18 and ART M19 were duplicate tests in which an artificial solution of 803 and magnesium was precipitated with ammonia. The 803 extractions in the sodium carbonate filtrates of these tests were 66.8 and 60.3 per cent. These are about the same extractions as were obtained in the tests of Table 2 on pure 803 solutions.

In Test ART M32 the artificial solution contained approximately 0.1 gram per liter 803, 1.2 gram ferric iron per liter and 0.4 gram aluminum per liter and was precipitated with ammonia. Treating the precipitate from this solution, which contained 0.4 gram aluminum per liter, with 32 equivalents of sodium carbonate resulted in 41.5 per cent extraction of 803. By increasing the aluminum to 4.0 grams per liter in the artificial solution, Test ART M33, the extraction in the resulting sodium carbonate filtrate was decreased to 3.2 per cent. It may therefore be concluded that the aluminum has a harmful effect on the carbonate extraction.

Precipitates from Leach Liquors

For Test 5M222, 1800 milliliters of leach liquor was precipitated with magnesia and filtered. Aliquots of the cake were weighed out. The effect of varying the equivalents of carbonate used is shown in Table 15. In this test an increase from 1.2 to 37.8 equivalents of carbonate increased 803 extraction from nil to 54.5 per cent. This test also showed a three-fold increase in extraction when the carbonate agitation period was increased from one hour to sixteen hours. In Test 5M226 (Table 15) the precipitation was carried out on six 500-milliliter samples of leach liquor individually. Here again, an increase in carbonate content increased the 803 extraction, but 64 equivalents gave only 37.5 per cent extraction.

Table 12. Carbonate Treatment of Oxidized and Non-Oxidized Sodium Hydroxide Precipitates from Artificial 803 and Ferrous Iron Solution

	Solution			Precipitation				Carbonate Retreatment				
	Analysis g/l					Aeration	Ppt.	Na_2CO_3			Agitation	
Test No.	803	Fe^{++}	Fe^{+++}	Reagent	pH	Time (Hours)	Wet Wt. g.	g.	Equiv.	pH	Time (Hours)	Extraction of 803, %
ART M16	0.100	1.2	0	NaOH	7.0	22	107.0	1.76	32	11.3	22	57.3
ART M30	0.090	1.05	0.07	NaOH	7.3	0	63.5	1.76	35	11.45	18	84.5
ART M37	0.090	1.05	0.07	NaOH	7.0	0	109.0	1.76	35	11.0	17	84.5

Table 13. Carbonate Treatment of Dried, Aerated, and Non-Aerated 803 and Ferrous Iron Precipitates

*ART M35	0.09	1.05	0.07	NH_4OH	7.5	0	Dried	1.76	35	--	18	50.7
ART M14	0.1	1.2	0	NH_4OH	7.5	22	63.0	1.76	32	11.3	22	57.3
ART M10A	0.1	1.3	0	NH_4OH	7.0	0	26.5	1.80	36	10.85	24	45.5

*Precipitate filtered and dried at 100°C, pulped with 100 ml. distilled water and treated with carbonate.

Table 14. Carbonate Treatment of Precipitates from Artificial Solutions Containing Magnesium and Aluminum

Test No.	Solution Analysis g/l SiO3	Mg	Al	Fe^{+++}	Fe^{++}	Precipitation Reagent	pH	% Recovery	Ppt. Wet Wt. g.	Carbonate Retreatment Na_2CO_3 g.	Equiv.	pH	Agitation Time (Hours)	Extraction of SiO3, %
ART M18	0.099	1.3	---	--	--	NH_4OH	7.9	95.3	8.0	1.76	32	--	22.5	66.8
ART M19	0.099	1.3	---	--	--	NH_4OH	7.4	98.1	10.0	1.76	32	--	22.5	60.3
ART M32	0.103	---	0.4	1.14	0.05	NH_4OH	7.15	99.2	117.0	1.76	32	9.6	24	41.5
ART M33	0.103	---	4.0	1.14	0.05	NH_4OH	7.1	99.4	305.5	1.76	32	8.45	18	3.2

Table 15. Sodium Carbonate Treatment of Magnesia Precipitates from Leach Liquor

Test No.	Solution Analysis g/l SiO3	Fe^{+++}	Fe^{+++}	Precipitation MgO	pH	Ppt. Wet Wt. g.	Carbonate Retreatment Na_2CO_3 g.	Equiv.	pH	Agitation Time (Hours)	Extraction of SiO3, %
5M222-A	0.109	0.37	1.01	L-2-35	7.0	12.5	0.065	1.2	--	1	--
5M222-B	0.109	0.37	1.01	L-2-35	7.0	12.5	0.52	9.5	--	1	2.4
5M222-C	0.109	0.37	1.01	L-2-35	7.0	12.5	0.52	9.5	--	16	7.5
5M222-D	0.109	0.37	1.01	L-2-35	7.0	7.5*	1.14	37.8	--	16	54.5
5M226-1	0.104	0.25	1.23	L-2-75	6.9	47.0	0.1	2	8.75	18	0.4
5M226-2	0.104	0.25	1.23	L-2-75	6.9	55.0	0.2	4	9.0	18	--
5M226-3	0.104	0.25	1.23	L-2-75	6.9	49.0	0.4	8	9.4	18	0.9
5M226-4	0.104	0.25	1.23	L-2-75	6.9	44.0	0.8	16	9.8	18	6.3
5M226-5	0.104	0.25	1.23	L-2-75	6.9	57.0	1.6	32	10.1	18	16.3
5M226-6	0.104	0.25	1.23	L-2-75	6.9	48.0	3.2	64	10.4	18	37.5

*Aliquot from 300 ml. leach liquor.

NOTE: Thirty-minute precipitation period in 5M222 precipitate filter cake used, carbonate agitation in open bekaers; in 5M226 thickened precipitate, carbonate agitation in closed bottles.

In Table 16, the effect of various precipitating reagents on SO_3 extraction from the precipitates of leach liquor is shown. The ammonia precipitate had the highest SO_3 extraction by sodium carbonate. Both the magnesia and lime precipitates had an appreciably lower extraction of SO_3 by carbonate. However, the magnesia was slightly better than the lime. None of the tests showed a good extraction of SO_3.

As extraction of SO_3 in the carbonate solution had increased with increase in sodium carbonate, a precipitate obtained with ammonia was treated with a large excess of sodium carbonate. The results are shown in Table 17. Even with 2.4 equivalents of sodium carbonate, the extraction of SO_3 in carbonate solution was under 50 per cent. Approximately 5.3 times the stoichiometric equivalent of sodium carbonate for the SO_3 plus ferrous iron present did not dissolve half of the SO_3 in 18 hours.

An attempt was made to oxidize all of the iron in the leach liquor to ferric iron by the addition of an excess of hydrogen peroxide before precipitation. This technique may have had other effects on the solution besides oxidizing the ferrous iron to ferric iron, for hydrogen peroxide forms an SO_3 complex similar to the carbonate complex. The precipitate appeared to be oxidized but no analysis for ferrous iron was made. Results of these tests are shown in Table 18. Even with the assistance of the peroxide complex the extraction of SO_3 from the precipitate did not improve. Test 5M235 showed a decrease in SO_3 extraction with increased agitation time.

In Tests 5M234A and 5M234B (Table 19), aeration after precipitation was employed to oxidize the ferrous iron to ferric iron. The four-hour aeration period may have been too short.

Table 16. Effect of Various Precipitating Reagents on SO_3 Carbonate Recovery from Leach Liquor Precipitates

	Solution			Precipitation			Carbonate Retreatment				
	Analysis g/l						Na_2CO_3				
Test No.	SO_3	Fe^{++}	Fe^{+++}	Reagent	pH	Ppt. Wet Wt. g.	g.	Equiv.	pH	Agitation Time (Hours)	Extraction of SO_3, %
5M226-6	0.104	1.23	0.25	MgO	6.6	48.0	3.2	64	10.4	18	37.5
5M228	0.104	1.23	0.25	CaO	6.4 - 5.0*	86.0	3.25	65	10.05	24	32.0
5M231	0.104	1.23	0.25	NH_4OH	7.0	191.0	3.25	65	10.25	16	54.0

*In Test 5M228 at one hour 6.4, at seventeen hours 5.0.

Table 17. Effect of Large Excess of Sodium Carbonate on Extraction of SO_3 from Leach Liquor Precipitate

50M19	0.0704	1.3	0.3	NH_4OH	7.15	123.0	8.25	214	10.7	18	43.2

Table 18. Carbonate Treatment of Precipitates from Leach Liquor Oxidized with Hydrogen Peroxide

5M232	0.104	1.23	0.25	NH_4OH	7.0	169.0	1.76	32	9.4	4	46.7
5M233	0.104	1.23	0.25	NH_4OH	7.0	251.0	0.44	8	8.4	4	10.8
5M235	0.104	1.23	0.25	NH_4OH	7.35	152.0	1.76	32	9.2	17	35.6

NOTE: 10 ml. 30 per cent hydrogen peroxide added before precipitation.

Table 19. Carbonate Treatment of Air-Oxidized Leach Liquor Precipitate with Sodium Carbonate and Ammonium Carbonate

5M234A	0.104	1.23	0.25	NH_4OH	7.0	159.0	0.055 1.55*	1 - 31	8.6	2.5	22.0
5M234B	0.104	1.23	0.25	NH_4OH	7.0	160.0	0.055 1.55*	1 - 31	8.6	4	22.0

*$(NH_4)_2CO_3$ 4 hours' agitation time in precipitation used for aeration.

A series of twelve tests (50M3-50M14) was run to determine the effect of the various carbonate compounds. Six liters of leach liquor was precipitated with ammonia to pH 7, and aerated 18½ hours while holding the pH at 7. The thickened pulp volume, after 4 hours' settling, was 1200 milliliters. Twelve 100-milliliter samples were pipetted to obtain the precipitate feed for the tests. Four series of three tests each were run, using a different carbonate solvent in each series: sodium carbonate, sodium bicarbonate, ammonium carbonate and a combination of sodium carbonate and ammonium carbonate. The concentrations of the carbonates were varied from 3 to 53 equivalents per one equivalent of the 803 present in the precipitate. Another series of 3 tests was run on precipitates obtained with sodium hydroxide. Results are given in Table 20.

Table 20. Carbonate Treatment of Air-Oxidized Precipitate from Leach Liquor with Different Soluble Carbonates

Test Numbers	Type Carbonate	Equivalents of Carbonate: 3	13	53
		% 803 Extraction from Precipitate		
50M16A, -B, -C	Na_2CO_3*	0.0	0.5	13.0
50M3, -4, -5	Na_2CO_3	0.5	11.9	50.0
50M6, -7, -8	$NaHCO_3$	0.4	10.9	10.9
50M9, 10, -11	$(NH_4)_2CO_3$	5.0	8.3	21.8
50M12, -13, -14	$(NH_4)_2CO_3$**	0.5	5.0	17.9

*Precipitated with sodium hydroxide.
**1.5 equivalents of sodium carbonate in these three tests in addition to the $(NH_4)_2CO_3$.

Leach liquor analysis: 0.063 g/l 803, 1.3 g/l ferrous iron, 0.17 g/l ferric iron.
Six liters leach liquor precipitated with ammonia to pH 7.2, aerated 18.5 hours, thickened, and 12 aliquot 100-ml. samples, 50M3 to 50M14, treated with carbonate for 16 to 17 hours.

The sodium carbonate gave the best 803 extraction. The sodium bicarbonate gave comparable results for the first two tests with low carbonate addition, but with the last increase in the concentration of sodium bicarbonate there was no improvement in 803 extraction. The ammonium carbonate and sodium carbonate plus ammonium carbonate gave lower 803 extractions than the sodium carbonate alone.

The aerated sodium hydroxide precipitates (Tests 50M16A, -B, -C) gave lower extractions of 803 with sodium carbonate than the ammonia precipitates.

This condition is not consistent with that found using artificial 803 and ferrous iron solution (Section V, Table 7), but is in accord with the results on artificial 803 and ferric iron solutions (Chapter III, Tables 3 and 4).

VI. ACID TREATMENT OF PRECIPITATES

In Topical Report A-25, Modified Leaching Process II was proposed for eliminating the iron from the leach liquor by precipitating at pH 5.5 or higher, aerating until all of the iron was oxidized to the ferric condition, and acidifying the pulp to pH 3.3 with sulfuric acid. The precipitated 803 would redissolve, while the iron would remain undissolved.

Two tests using this principle were run on an artificial 803 and ferrous iron solution. Results are shown in Table 21.

Table 21. Acid Treatment on Oxidized 803, Ferrous Iron Precipitates

Test No.	Precipitate Reagent	pH	Aeration Time (Hours)	Acidified to pH	Time in Acid (Hours)	% Extraction in Acid Filtrate
ART M26	NH_4OH	7.6	23	3.15	0.16	6.4
ART M27	NH_4OH	7.8	23	2.9	23.0	75.0

Leach liquor analysis: 0.090 g/l 803, 1.05 g/l ferrous iron.

NOTE: Test ART M27, nil iron in acid filtrate. Precipitate settled in acid twenty-one hours, agitated two hours, pH crept up from 3.0 to 4.1. Acid added again, pH held at 2.9 for two hours' agitation.

Agitation time was two hours after the precipitate had settled in acid solution twenty-one hours. There was no iron in either of the acid filtrates.

The next test was run using an artificial solution of ferric iron and 803. The ammonia precipitate of 803 and ferric iron was filtered, the filter cake pulped in distilled water, treated with sulfuric acid and agitated seventeen and one-half hours at pH 2.9. The 803 extraction in the acid filtrate of this test, ART M39 was 86.2 per cent, and the iron content was nil.

Four tests were then run using 396-50 leach liquor, precipitated to pH 7 with ammonia, aerated, and filtered. The precipitates were repulped with distilled water, agitated with sulfuric acid seventeen and one-half hours at pH 2.5 to 3, and filtered. A sample of each acid filtrate was analyzed for 803. The first acid filtrate was also analyzed for iron, aluminum, silicon, and magnesium. The remainder of the acid filtrates were reprecipitated to pH 7 and treated with sodium carbonate. Results are shown in Table 22.

Table 22. Carbonate Treatment of Acid Filtrate from 803 Precipitates

Test No.	% 803 Recovery in Acid Filtrate	% 803 in Acid Residue*	Precipitating Reagent	pH	Na_2CO_3 Added to Re-Ppt. Pulp g.	Na_2CO_3 Added to Re-Ppt. Pulp Equiv.	pH	Na_2CO_3 Agitation Time (Hours)	% 803 Extraction from Acid Filtrate	Total 803 Recovery %
50M20A	74.0	0.364	--	--	--	--	--	--	--	--
50M20B	69.4	0.398	NH_4OH	7.15	3.52	80	10.05	17.5	59.6	41.4
50M20C	77.7	0.359	NH_4OH	7.35	10.56	206	10.45	17.5	65.2	50.7
50M20D	73.7	0.336	Na_2CO_3	7.55	3.52	70	10.3	17.5	102.2	75.3

Leach liquor analysis: Four samples precipitated with ammonia to pH 7, aerated 20 hours, filtered, precipitate filter cake pulped in 150 ml. distilled water, acidified with sulfuric acid to pH 3, agitated 17.5 hours, and filtered. Sample A - complete acid filtrate analysis: 0.183 g. 803, trace iron, 0.37 g. alumina, 0.37 g. silica, nil magnesia per liter. Samples B, C, and D - 250 ml. acid filtrate reprecipitated and treated with sodium carbonate.

*Ignited basis.

The extraction of SiO_3 in the acid filtrate was between 69.4 and 77.7 per cent. Most of the silica and alumina from the leach liquor are contained in the acid filtrate. Precipitation of this filtrate with ammonia gave milky-white, viscous precipitate. Treatment of this precipitate with 80 equivalents of sodium carbonate gave 59.6 per cent extraction of SiO_3 in the carbonate filtrate, while treatment with 206 equivalents increased the SiO_3 extraction to 65.2 per cent. However, when the acid filtrate was neutralized by precipitation with sodium carbonate and the precipitated pulp treated with an additional 70 equivalents of sodium carbonate, the assay showed that all of the SiO_3 in the acid filtrate was recovered in the sodium carbonate filtrate.